Vision of the U.S. Biofuel Future: A Case for Hydrogen-Enriched Biomass Gasification

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Researchers at the Forest Product Laboratory (FPL) and the University of Wisconsin−Madison (UW) envision a future for biofuels based on biomass gasification with hydrogen enrichment. Synergisms between hydrogen production and biomass gasification technologies will be necessary to avoid being marginalized in the biofuel marketplace. Five feasible engineering solutions have been suggested for this synergism. We are researching one solution to investigate cleaner and more-efficient wood gasification via high-temperature liquid metal as a carrier fluid and making use of hydrogen, power, and waste heat from future nuclear reactors. The enrichment of syngas with nuclear, windmill, or solar hydrogen permits full conversion of all carbon from biomass to produce competitive synthetic gasoline, diesel, or other liquid hydrocarbon or alcohol fuels.

Introduction

Futuristic productions of hydrogen or biomass synfuels by themselves are threatened to be marginalized in the motor fuel market sector if the coal-to-liquid (CTL) technologies now being commercialized are able to produce diesel at a cost of $1/gal at the plant gate.[1] In this paper, we show how separate productions of hydrogen fuel and biomass-based synfuel are unlikely to be able to compete with CTL synfuels, whereas the synergistic biomass gasification with hydrogen enhancement for conversion to synfuel can eventually reach the competitive level of $1/gal diesel. Indeed, if the carbon dioxide sequestration costs were to be added eventually to the costs of producing synfuel, then the hydrogen-enhanced biomass synfuel should become more cost-competitive. In addition, we show how the increased productivity due to the hydrogen-enhanced biomass biofuel can lead to full displacement of the annual U.S. fossil fuel consumption in the transportation sector. This synergistic approach will be observed to have several other benefits, including the elimination of the global heating gases contribution, which we will list in Appendix A. The newness of this concept is indicated in that only one other reference (Agrawal et al.[2]) was found for promoting hydrogen enrichment of biomass gasification. In this paper, we demonstrate that the evolution of biomass gasification technology will necessarily proceed in this direction and that there are several alternative engineering solutions for the process.

To rationally build the case for hydrogen-enriched biomass gasification, we begin, in the first section, by explaining the woody biomass feedstock composition, the fundamental processes for wood pyrolysis, and the steps needed to achieve the difficult gasification of various pyrolysis products—noncondensable gases, light and heavy tar, and char—and their conversion into a syngas suitable for synthesis to liquid transportation fuel. Because biomass gasification technologies have been improving in their ability to gasify the carbon in the biomass completely, there arises the challenge of converting as much of that carbon as possible into the liquid synfuel. The use of external hydrogen can make this possible as (1) a fuel in the burners, (2) a reactant (to more easily convert the carbon to a gaseous form), and (3) a diluent to increase the H_2/CO gas molar ratio needed by the Fischer−Tropsch reactions. That is, the process avoids using the water−gas shift typically used with biomass that unnecessarily increases the CO_2 levels. Furthermore, the oxygen obtained from splitting the water, instead of from nitrogen-laden air, can be used to help gasify the char to produce, primarily, the CO needed for syngas. The second part of the paper analyzes these factors on the basis of feedstock costs and productivity, to show that, indeed, the conceptual use of external hydrogen from the splitting of water is quite beneficial and that we should try to increase synfuel productivity from biomass to the maximum extent possible. After understanding the goals to be achieved with hydrogen-enhanced biomass gasification, it provides a guiding principle in which to examine, improve, and promote compatible technologies for biomass gasification and hydrogen production. This leads to the third major section of this paper, in which five possible engineering solutions are suggested for consideration by the bioenergy community. Three of the engineering solutions are based on direct extrapolation from current commercial processes, while the last two engineering solutions are being researched between our two institutions.

Biomass Resource Characterization

In this study, we characterize lignocellulosic biomass as ∼30% lignin (by weight) and ∼70% carbohydrate polymers (holocellulose), in the form of hemi-cellulose (polymers of C5 and C6 carbohydrates that are readily hydrolyzed to form simple sugars) and cellulose (mainly glucose polymers that are more difficult to hydrolyze). For approximate analysis, we assume holocellulose to have the empirical formula $C_6H_{10}O_5$ and the lignin to have the empirical formula $C_9H_6O_2(H_2O)(OCH_3)_{4/3}$,

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which has a close correlation to their measured and calculated heat of combustion values.[3] If we further "conceptually" reduce the wood structure to monomer units given by the empirical formula and on a moisture-free, ash-free, and extractive-free basis, the molar fractions of lignin and holocellulose are, respectively, 25% and 75%. This gives the overall empirical formula for the generic dry lignocellulosic biomass as $C_6H_{8.9}O_{4.1}$, which is in close agreement with that which is used by the biomass community ($C_6H_9O_4$).[4] This allows identification of "typical" woody materials with the more general class of biomass materials, including wood bark wastes, forest residues, wood byproducts, agricultural wastes, urban yard wastes, and even some municipal refuse biomass wastes.[5] However, the materials would vary in their mineral contents, which end up mostly in the ashes of a fully gasified biomass. The presence of sulfur is related to fossil sources such as coal and petroleum and to paper pulping in the form of black liquor. Any sizable nitrogen content is identified with organic wastes and municipal refuse biomass wastes, rather than the woody or agricultural biomass that provides most of the 1.36 billion tons per year of biomass potentially available in the United States for conversion to biofuel.[6]

Background Information on Wood Pyrolysis and Gasification

Fundamental mechanisms of wood pyrolysis and gasification provide important clues to understanding the difficulty and possibility for producing syngas from biomass. Here, we define syngas loosely as a mixture of primarily CO and H_2 with minor components of H_2O, CO_2, CH_4, N_2, and higher hydrocarbons than methane. The forerunner to the syngas or synthesis gas end-product might also be defined as producer gas. Generally, the heat value of syngas is maximized when H_2O, CO_2, and N_2 are either removed or prevented from developing, and also when the H_2:CO ratio is maximized.

The wood gasification process begins conceptually with "dry distillation" (traditionally associated with slow heating rates at low temperatures), where the H_2O is mainly removed from the wood structure and we are left with a dry charcoal that mostly retains the combustion heat of wood, because the emitted steam has no heat of combustion. The dry distillation process can also be completed in a matter of minutes with other volatile gases emitted besides steam, such as when wood particles are drawn between two 80-mesh stainless steel screens immersed in low-temperature liquid metal alloy, at temperatures of 200−360 °C, depending on the quality of charcoal desired (see the 1949 patent by FPL researcher Alfred J. Stamm[7]). Temperatures of >360 °C were evidently avoided by Stamm,[7] because it would have corresponded to breakdown of the lignin, which would result in phenol-based molecules within a tar that would have a greater tendency for gumming the process. The breakdown of lignin and release of phenol-based molecules at lower temperatures (<360 °C) is reduced by the absence of free moisture and air,[8] which must be removed to avoid production of such gumming tar components. Furthermore, it can be noted that a fast pyrolysis process is more easily achieved with the prior removal of free moisture, because of the high loading of evaporative heat.

The next conceptual step is char gasification with steam by borrowing the appropriate technology from charcoal gasification[9] to produce high-quality and approximately equimolar concentrations of CO and H_2 at a temperature of ∼1100 °C and pressure of 1.0 bar (with lower heating value of 12.65 MJ/m^3). Excessive steam levels will promote the water−gas shift reactions, $CO + H_2O \rightarrow CO_2 + H_2$, which will have the effect of reducing the heat value of syngas unless steam can be condensed and CO_2 can be removed via a separation process. The drawbacks to this approach include the large endothermic heating required (using at least one third of the fuel value, or using solar irradiation or nuclear energy instead as a heat source, as suggested by Muller et al.[9]), the very slow reaction rates of carbon gasification by steam (as compared to direct pyrolysis), and/or H_2 sparging of the residue and the need for an external source of water for the reaction processes.

If, instead of dry distillation, the typical dried biomass is dramatically heated to 400−600 °C, then the pyrolysis should produce (by weight) ∼70% tar and ∼10% gas within the wood volatiles, with ∼20% remaining as char (mostly carbon and ash), which is a typical situation for wood fires. Because the volatiles produced under these conditions have a tendency to have the overall empirical formula $(CH_2O)_x$,[10] we know, from the equilibrium chemical balance at 1000 °C and 1.0 bar, that the volatiles will reduce to equimolar concentrations of CO and H_2,[9] which is a very clean "medium calorific value (MCV)" syngas (if one could approach the equilibrium conditions). In an efficient process that gives higher-heat-value syngas, one would want to combust the char in an external chamber to heat a heat carrier such as sand, which can be circulated into the gasifier chamber for fast heat pyrolysis of the biomass. If excess heat from such combustion is present, some of the char can instead be gasified endothermically with steam to produce additional equimolar CO and H_2 to mix with the volatiles. Excess steam needed for this process also has the side effect of increasing the H_2:CO molar ratio in the raw syngas via the water−gas shift reaction, but at a penalty of somewhat reduced heat of combustion, because of the resulting increased CO_2 levels.

Efficient production of MCV gas at 1.0 bar without active use of oxygen to crack the tar conventionally requires a circulating fluidized bed (CFB), which uses circulating sand/catalysts and steam injection from the bottom of the gasifier chamber into the biomass feedstock. A cyclone separates hot sand/catalysts from the flue gas (see the description of the biomass plant in Güssing, Austria reported by Hofbauer[11]). The Battelle gasifier[12] similarly uses a conveyer for rotating sand between pyrolyzing and combustion chambers, so that it also produces MCV gas. We note, in passing, that these and other examples of CFB concepts usually require separation devices for cleaning out residual tar, soot, and undesirable gases in the exiting "crude" syngas that has not been able to reach equilibrium at ∼1000 °C and 1.0 bar. There are also other concepts to achieve fast pyrolysis of biomass and the corresponding MCV syngas at atmospheric pressures, but most of them cannot contend with the gumming of the processes by the constantly changing tar component, or efficiently address the char component. This is where the sand as a heat carrier has an advantage, in which gummed char on the sand particles is combusted and then the hot cleaned sand circulates. This is again a reason why we would not consider a much higher temperature version of Stamm's invention for making charcoal, because of the possibility for gumming the separation screens by the changing tar, or by a fatigued failure of such metal screens at very high temperatures in our attempts to gasify the char. We would still consider the molten metal component as heat carriers that can maintain uniform temperatures throughout better than beds of sand.

Conceptual Improvements via Flash Pyrolysis

One possible improvement over these fast pyrolysis "MCV syngas" technologies involves flash pyrolysis (very rapid

Table 1. Net Reaction for Woody Biomass ($C_6H_9O_4$) to Ethanol (C_2H_5OH)

technology of gasifier/synthesis	biomass energy (%)	Amount of Component (mol)				fuel production (gal/dry ton)
		H_2	C_2H_5OH	H_2O	CO_2	
current CFBs with flue output	50	0	1.04	−0.88 2.25	0.92 3.0	100
self-sufficient heat with flue output	80	0	1.66	−1.4 0.9	1.46 1.2	161
use external heat and external water	100	0	2.08	−1.75 1.75	1.83	202
use external heat and external H_2	144	−5.5 5.5	3	1	0	291

pyrolysis of biomass). If dried generic biomass can be pyrolyzed into gaseous form completely by an idealized flash pyrolysis process, then the chemical makeup of lignin and holocellulose leads conceptually to the formation of additional methane in the syngas, and an overall heating value of 20.0 MJ/m^3 as a limit (the overall heating value of pure methane is 38 MJ/m^3). Indeed, past research on flash pyrolysis and gasification of selected wood species (mixtures of 90% birch and 10% aspen or 25.4% lignin and 74.6% holocellulose (by weight), using the aforementioned monomer empirical formula as a fit to the ultimate data provided by Chen et al.[13]) demonstrated interesting results. Under flash pyrolysis conditions, the yield of char reached an averaged value of 10.4% and was independent of (1) the fluidizing gases, (2) pressures of >1.0 bar, and (3) temperatures of >650 °C. The overall char yield of 10.4% corresponds to 41% and 0%, respectively, for char yields of lignin and holocellulose of the selected wood. These results are also in agreement with existing data on flash pyrolysis of cellulose and lignin as isolated components.[14]

Following these observations, researchers have sought to optimize the gasification of char at 700 °C by inserting steam at the same time as the flash pyrolysis event (before the char anneals and becomes much less reactive) and by raising the pressure to at least 10 bar. At this level, the conversion rate of char increased to 4%/min.[13] This led to consideration of a pressurized fluidized-bed reactor to improve on some existing technologies. However, because steam/oxygen was required for char gasification, the significant potential increase in the heating value was not realized, particularly if the steam also reacted with carbon-enriched tar. There is also the economical problem of a pressurized gas system, unless the use of syngas requires it anyway, such as powering a fuel turbine. This also describes the GTI/IGT RENUGAS process that uses a 20-bar pressurized bubbling fluidized-bed process.[15]

Goals for Hydrogen-Enriched Full-Carbon Gasification

Because the Fischer−Tröpsch synthesis (FTS) reactions are relatively inert to N_2, CO_2, CH_4, and H_2O and generally require H_2:CO ratios of ∼2 (as reactants to form synfuel, H_2O, and/or CO_2), it is beneficial to (i) upgrade the raw syngas via the very endothermic reforming of methane ($CH_4 + H_2O \rightarrow 3H_2 + CO$ and/or $CH_4 + CO_2 \rightarrow 2H_2 + 2CO$), (ii) provide any needed exothermic water−gas shift, (iii) separate out the excess "inert" gases, and (iv) remove contaminants that deactivate the catalysts.[16] The current commercial FTS catalysts are known to provide ∼80% conversion of the CO to synfuel, although recent literature shows multistage strategies and new catalyst developments to boost conversion efficiencies and selectivity and overcome short deactivation times and excessive attrition rates. However, this upgrading of syngas is a major cost issue for implementing a biorefinery based on conventional technology. Indeed, the many steps required to achieve the adequately purified syngas result in using up ∼50% of the biomass combustion energy with conventional technologies. Just using the heat of enthalpy data for each molecule involved in the net reaction for wood gasification to syngas ($C_6H_9O_4 + 2H_2O \rightarrow 6CO + {}^{13}/_2H_2$), the amount of endothermic heat required is calculated to be 23% of the wood combustion heat. The other 27% of the biomass energy that is combusted or wasted with the conventional technology can be greatly reduced by revamping the gasifier design, increasing process conversion efficiencies, and achieving energy-conserving processes, such as those suggested with the use of liquid-metal-based gasification.

Because the FTS reactions release heat that is equivalent to ∼29% of the wood feedstock combustion heat, it may be beneficial to reduce the gasification temperature using catalysts down to that of the process temperature (230−340 °C) for FTS, so that its heat can be directly transferred to gasify the feedstock. Thus far, this severe reduction in gasification temperature has only been proven with a small throughput catalyst, using pure glycerol in aqueous solutions as the feedstock.[17] A viable alternative to reducing the gasification temperature is the provision for an inexpensive source of H_2 from the splitting of water for combusting with O_2 in the gasifier chamber, which provides the process heat needed to generate purified syngas. This would mean that none of the biomass is combusted to provide process heat, and that 100% of the biomass combustion heat is converted to FTS products (that is, in the case of the idealized net reaction of wood syngas to iso-octane, $6CO + {}^{13}/_2H_2 \rightarrow {}^1/_2C_8H_{18} + 2CO_2 + 2H_2O$, ∼94% of the biomass combustion energy goes into the synfuel portion). Obviously, the amount of external H_2 utilized for the process heat can be minimized with the revamping of gasifier design and achieving energy conservations. We note that the 100% biomass energy conversion of $C_6H_9O_4$ into iso-octane results also in the process emission of 2 mole units of CO_2. However, this emission can be prevented by merely enriching the wood syngas directly with external hydrogen (${}^{25}/_4$ mole units of H_2) to produce the idealized FTS product at the 150% biomass energy conversion (as ${}^3/_4C_8H_{18} + 6H_2O$) instead. The 6 mole units of H_2O FTS product is then recycled into a water splitting unit to provide a portion of the "external" H_2 for process heat and syngas enrichment and provide O_2 for assisting tar cracking and/or char gasification. The other "external" H_2 and O_2 are derived from the splitting of moisture evaporated from the green wood. This very significant enhancement, along with converting all biomass carbon to synfuel, should triple the fuel productivity of current biomass gasification technology (fuel output per unit of biomass input). In the next few paragraphs, we will show that it is worth the effort to improve the gasifier to the maximum possible with H_2 enrichment.

Because current gasifiers are far from approaching the theoretical limits of fuel productivity, we show, in Table 1, four alternative levels of gasifier/synthesis productivity (i.e., the ratio of FTS products energy to the woody biomass energy, expressed

Table 2. Net Reaction for Woody Biomass ($C_6H_9O_4$) to Iso-octane (C_8H_{18})

technology of gasifier/synthesis	biomass energy (%)	Amount of Component (mol)				fuel production (gal/dry ton)
		H_2	C_8H_{18}	H_2O	CO_2	
current CFBs with	50	0	0.25	0	1.0	68
flue output				2.25	3.0	
self-sufficient heat	80	0	0.4	0	1.6	109
with flue output				0.9	1.2	
use external heat only	100	0	0.5	0	2	136
use external heat	150	−6.25	0.75	4	0	204
and external H_2		6.25				

Table 3. Net Reaction for Woody Biomass ($C_6H_9O_4$) to Diesel ($C_{15}H_{32}$)

technology of gasifier/synthesis	biomass energy (%)	Amount of Components (mol)				fuel production (gal/dry ton)
		H_2	$C_{15}H_{32}$	H_2O	CO_2	
current CFBs and	50	0	0.136	0.076	0.962	62.1
flue output				2.25	3.0	
self-sufficient heat	80	0	0.217	0.122	1.54	99.4
and flue output				0.9	1.2	
use external heat only	100	0	0.272	0.152	1.92	124.2
use external heat	147	−5.9	0.4	4	0	182.8
and external H_2		5.9				

as a percentage, with ethanol as the primary synfuel). As already mentioned, conventional gasifiers (see the "current CFBs with flue output" entry in Table 1) are operating at a level of, at most, 50% conversion of biomass energy to ethanol, because at least half of the molar carbon from biomass is emitted in the flue as CO_2; that is why they can only theoretically produce, at most, 100 gal of ethanol per dry ton of woody feedstock. Conventional gasifier/synthesis produces almost 1 mol of CO_2 and ethanol per empirical mole unit of biomass from the FTS reactions. Since 0.88 mol of H_2O is used in the ethanol reaction, it will require some condensate from the flue gas, which is producing 2.25 mol of H_2O. Note that, with 3 mol of CO_2 in the flue gas, the conventional gasifiers generate ~4 mol of CO_2 for each mole of ethanol produced.

Going to the next higher level of fuel productivity (see the "self-sufficient heat with flue output" entry in Table 1), it should be possible to improve biomass energy conversion to 80% with a new design, so that there is a much-reduced 1.6 mol of CO_2 generated per 1 mol of ethanol. However, even with condensate from the flue gas, at least 0.3 mol of external water per 1 mol of ethanol is being consumed. The benefit is producing 161 gal of ethanol per dry ton of woody biomass. We can continue to improve the gasifier/synthesis by now utilizing external heat, such as that from nuclear energy or solar heat or combustion of external H_2 (see the "use external heat and external water" entry in Table 1). At 100% biomass energy conversion (as we defined earlier), we have significant use of external water, on the order of ~1 mol of H_2O per 1 mol of ethanol, to produce ~1 mol of CO_2 per 1 mol of ethanol, which is coming out at 202 gal per dry ton. Finally, as shown in the last line of Table 1, if we get sufficient nuclear or solar H_2 gas to provide for both process heat and reactant, the gasifier/synthesis productivity should then reach its ultimate limit of 3 mol of ethanol, 1 mol of H_2O, and zero process CO_2 emission to produce 291 gal of ethanol per dry ton. Similar idealized constructions are provided for woody biomass conversion to gasoline and diesel fuel in Tables 2 and 3, respectively.

In Figure 1, we look at the similar net chemical reactions for the case of producing diesel, with the formula $C_{15}H_{32}$, as it varies with biomass energy percentage. We can see that it is beneficial, from the ecology standpoint, to nudge gasifier productivity to higher values. For example, at 100% biomass energy conversion to FTS products, the need for oxygen (filled triangle points) to oxidize with biomass is, by definition, zero; the production of water (filled diamond points) decreases to a small 2% emission, the production of CO_2 (filled square points) is reduced to 58% emission, and the diesel output (filled circle points) increases gradually to 40% of the biomass (by weight).

At the theoretical limit of the gasifier/synthesis conversion of biomass, which for diesel is 147%, all of the carbon in the biomass is converted to diesel and there is no process CO_2 emission. A net input of 24% moisture content of biomass is sufficient to provide water for splitting into H_2 and O_2 via energy from external sources (not biomass). Because the H_2 is incorporated into the diesel fuel (58% net emission), there will be a net emission of O_2 at 65% (by weight). All of the emission quantities obviously have a linear relationship, from 50% to 147% of the biomass energy.

From Tables 1−3, we have plotted the corresponding idealized fuel production (as gallons per dry ton of woody biomass) versus the percentage of biomass energy in Figure 2. From this plot, the shipping and storage costs for diesel and gasoline obviously would be much lower, in comparison to ethanol, for the same amount of fuel energy value.

When the biomass-based biofuel industry expands in the future and the demand for biomass increases, the cost of biomass feedstocks will inevitably escalate (as a matter of supply and demand). We estimate that a realistic long-run value for delivered biomass feedstock is $75 per dry ton (by extrapolating from the data of Walsh,[18] for a reasonable crop yield of hybrid poplar for various regions and adding in costs for transportation and an inflation factor). We believe that lower feedstock values (at approximately $45 per dry ton) may be obtained initially when the biofuel industry is in its infancy; however, when the industry ramps up to larger-scale production, the cost of biomass feedstock will increase. This likely escalation of biomass feedstock cost is also implicit in the recently published Billion Ton Biomass report, which projected that ~1.36 billion dry tons of biomass could be available in the long run in the United States for use in biofuels, but it would require the cultivation and development of dedicated biomass energy crops, such as short-rotation hybrid poplars, willows, and switchgrass. We assume that a sustainable long-run cost for such feedstock crops will be approximately $75 per dry ton delivered.

Therefore, using data from Figure 2 and the $75/ton biomass cost assumption, we can calculate the biomass supply cost per gallon of synfuel at different levels of biomass energy percentage, the results of which are shown in Figure 3. For diesel, the

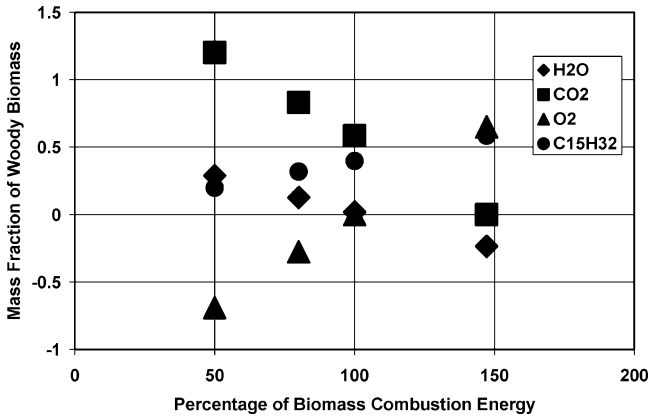

Figure 1. Net process emissions of CO_2, H_2O, O_2, and diesel from woody biomass.

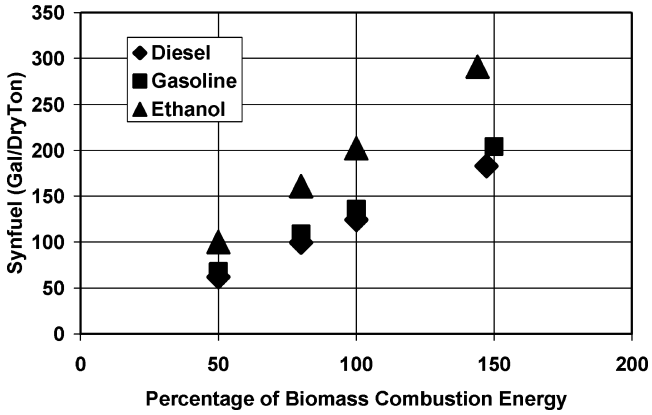

Figure 2. Potential synfuel productivity from woody biomass, as a funciton of gasifier efficiency.

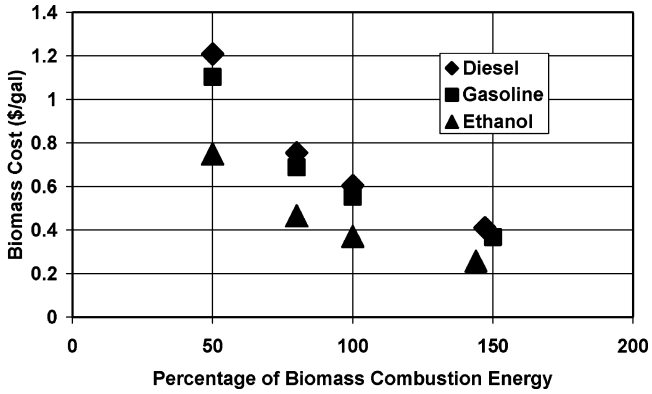

Figure 3. Delivered biomass cost at $75 per dry ton, converted to feedstock cost per gallon of synfuel.

cost of biomass supply ranges from $1.21/gal at the current 50% biomass energy level to $0.60/gal at the 100% biomass energy level, and to just $0.41/gal at the 147% biomass energy level. Compare this to the anticipated CTL cost of $1/gal diesel at the plant gate. Although ethanol has a much lower cost, in regard to cost of biomass supply per gallon, the lower energy value and higher shipping cost of ethanol cancel that advantage.

For a more complete economic assessment of feedstock (input) costs, we show, in Figure 4, the combined total cost of H_2 and biomass feedstock involved in producing diesel at different levels of biomass energy percentage. We believe it is wasteful to isolate H_2 from biomass or synfuel to use as a hydrogen feedstock, because it will be more efficient to convert most or all carbon in the biomass into synfuel using external sources of hydrogen. We note that a short-term goal for the

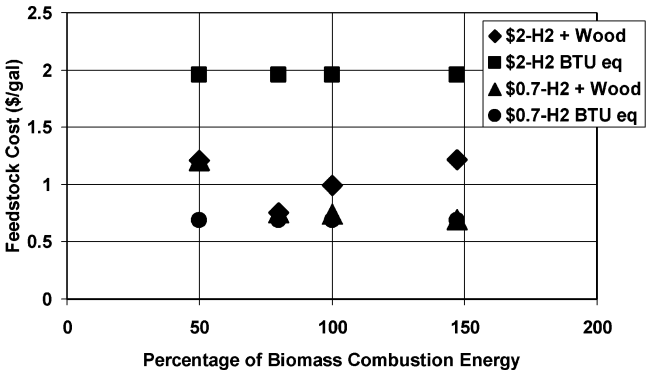

Figure 4. Feedstock cost per diesel gallon for $75 per dry ton of woody biomass and $0.70/kg to $2/kg of "green" H_2.

hydrogen industry[19] is to obtain $2/kg of "green" H_2 at the plant gate, and then add a dollar more per kilogram to ship the H_2. This converts, in terms of equivalent LHV at the plant gate, to $2/gal of diesel fuel, as shown by the square points. The levels at 50% and 80% of biomass energy do not need H_2 as input, but they will have biomass feedstock costs that are much less than what the H_2 near-term technology can provide. Further examination of the U.S. Department of Energy (DOE) website[19] indicates the possibility of $1/kg of H_2 at the plant using windmill power for the electrolysis of water, when co-producing power for the electricity grid. It is interesting that, if, in the far future, the cost of H_2 decreases to $0.70/kg, we will have a situation that it might be fruitful to develop a new infrastructure to use hydrogen directly as transportation fuel, provided, of course, that we are stuck at the 50% biomass energy conversion level with the bio-chemical approach or with current gasifier technology, or that the CTL diesel ultimately costs much more than the anticipated $1/gal. However, if we increase fuel output to reach 150% of biomass energy (needing at least 5.9 mol of external H_2 per mole of $C_6H_9O_4$), it will be more efficient, in terms of total feedstock costs, to incorporate manufactured H_2 into the synfuel, even when H_2 is available at $0.70/kg, and also to avoid being forced to develop the costly H_2 infrastructure.

As shown in Figure 4, the total feedstock cost is $1.21 per gallon, regardless of whether we are at 50% biomass energy or at 150% biomass energy, using the $2/kg H_2. However, the 3-fold increase in synfuel productivity will reduce capital costs and provide greater potential for profit. We emphasize that this would occur while paying biomass providers $75 per dry ton of woody biomass delivered, which should be enough to encourage them to practice resource sustainability and permit government to conserve prime woody biomass for ecological development of habitat, watershed, and biodiversity. Because we can expect the H_2 far-future production to fall below $1/kg, the combined feedstock costs of biomass and hydrogen, on the basis of the cost per gallon of diesel, will leave plenty of room for capital and operational costs to finally reach the targeted $1/gal of diesel to compete with CTL or petroleum sources of motor transportation fuel.

Therefore, in anticipation of the coming hydrogen economy, we will want to build a gasifier that can function at up to a level of 150% as we begin to add components related to the use of hydrogen gas that aids in the total conversion of biomass carbon to synfuel. This would be a real advantage, in comparison to some existing gasifiers, which must undergo expensive replacement or upgrading to remain current with the advances in the H_2 production and biomass carbon conversions. Indeed, the possibility of future low-cost H_2 enrichment of gasified biomass may make for a serious competition with biorefineries

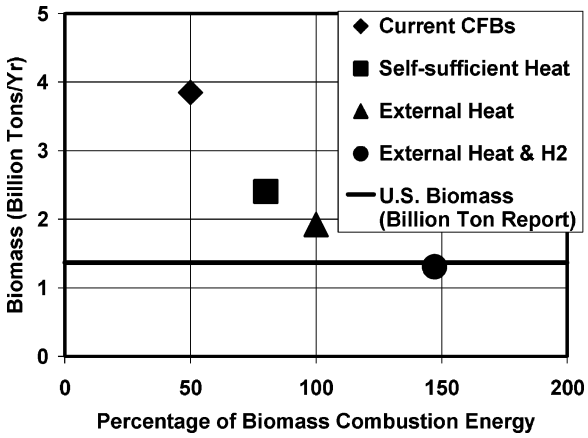

Figure 5. Biomass required to displace U.S. oil consumption (5 billion barrels/yr) for transportation.

that involve expensive catalysts or genetically engineered organisms for processing woody biomass into biofuel, particularly if the use of external sources of water and large processing plant footprints can be avoided.

Potential for Replacing Fossil Fuels with Biofuels in U.S. Transportation

Another question we address is whether the United States has sufficient biomass to replace fossil fuels in transportation. It has been estimated recently that the volume of biomass that we can modestly obtain without affecting any other crop or forest usage, as described in the Billion Ton Report,[6] is 1.36 billion dry tons per year for the United States. We note again that this level of biomass production is likely to be economically obtainable only if prevailing biomass prices reach $75 per dry ton of biomass delivered to plant.

At the conventional 50% biomass energy level, as shown in Figure 5, this 1.36 billion tons of biomass is only one-third of that needed to displace the 5 billion barrels of petroleum consumed per year for transportation fuels in the United States.[20] Note that 5 billion barrels of petroleum was converted to 3.9 billion tons of biomass using the synfuel production data in Tables 1−3 for the 50% biomass energy level. This result is in agreement with various other studies, including that by Purdue University.[2] However, if we move to the 147% biomass energy level, which relies on the use of "green" H_2 and the conversion of all feedstock carbon to synfuel, we could provide for all of our liquid fuel transportation needs via biofuels produced from 1.36 billion tons of biomass. If we also significantly improve our gas mileage, we can entertain the thought of becoming an energy-exporting nation and actually take carbon out of the atmosphere, because we leave the plant roots and some leaves in the ground. This presents a golden opportunity to jump start the hydrogen and biofuel economy without having to develop long-term exotic technologies that involve genetic, catalyst, or nanostructure engineering. Now that we can envision our biofuel production goal, we should seek to reach it with innovative concepts to produce synfuel that involves hydrogen-enriched biomass gasification and with catalyst synthesis of the upgraded syngas.

Developing Gasification Technologies for Complete Conversion of Biomass Carbon

The literature was searched for gasification technologies that have the potential to completely convert the biomass carbon to the gaseous state (this is called the producer gas). More-detailed descriptions of some of these gasification technologies are in a report on the DOE website;[21] this report is their literature survey. The potential for gasification technologies to also convert the producer gas to high-quality syngas was included in this evaluation. Because of the preponderance that gasification technologies involve the combustion of some portion of the biomass to obtain the process heat needed to produce the syngas, the vast majority of gasification technologies are excluded. For example, the downdraft and updraft gasifiers may produce relatively clean producer gas (free of tar, soot, or other contaminants) but they have low BTU values, because of the partial combustion of some pyrolysis products in the presence of producer gas. This will mean that the excessive amount of CO_2 and N_2 will have to be expensively removed to upgrade the producer gas to syngas. The CFB or the bubbling fluidized bed technologies rely on the use of a moving heat carrier, such as sand, in which some unconverted tar and char are deposited. Combustion of these deposits is done in a separate chamber to retain the performance of such heat carriers and to prevent the development of CO_2 and N_2 within the producer gas in the gasification chamber. However, there remains a considerable amount of tar and char particles within the MCV producer gas that must be expensively removed or reformed during the upgrade to syngas. Also, these fluidized-bed technologies invariably lose some biomass carbon into the flue exhaust. Indeed, few gasification concepts remain (i) if we require that the process heat can be obtained solely with the H_2 combustion heat source, and (ii) if the correspondingly displaced carbon can then be efficiently gasified into hydrocarbons or carbon oxides, for later conversion to syngas. This is the fundamental reason why many current gasifiers cannot approach the 150% gasifier conversion efficiencies.

In the following discussion, we select three promising commercial-level gasification technologies for further evaluation, with a view toward evaluating other gasification technologies, as well as providing a springboard to develop the entirely new gasification concepts. This discussion is not intended as a promotion of these or other gasification technologies, but rather to provide an evaluation methodology. These particular technologies have already demonstrated the almost-complete conversion of biomass carbon into the gaseous state. The discussion will explain how that is achieved and also evaluate the potential for their upgraded syngas and their compatibility with a current H_2 generation technology. The fact that the selected technologies are based on entirely different gasification processes may suggest a hybrid-type technology that has the best of their features while circumventing the negative or uneconomical features.

Low-Temperature Atmospheric-Pressure Steam Pyrolysis and Gasification, Followed by Methane Reforming. The first example involves low-temperature atmospheric-pressure steam pyrolysis and gasification, followed by methane reforming, as proposed by ThermoChem Recovery International, Inc. (TRI).[22] The pyrolysis occurs on a steam fluidized bed and the tar cracking/gasification occurs on the exterior, on tubes that are heated from within via a pulsed combustion process. The char is converted in a commercial unit that involves partial air combustion to make CO to mix with the producer gas. Although natural gas is presently used as fuel in the combustor, there seems to be no difficulty in regard to, instead, using purely H_2 gas or the combustible tail-gas from the FTS reactions. Therefore, the amount of biomass carbon lifted into the producer gas is almost complete, although there is a considerable amount of methane and CO_2, and still quite a bit of tar, solid carbon, and contaminants. Because the endothermic methane reforming

to syngas is done with a possible steam addition at ~800 °C on the metal catalysts in a separate heated chamber, this requires that the producer gas be first cooled somewhat and the contaminants, tar, and solid carbon be cleaned out, to avoid deactivating the methane reforming catalyst. This multistage process of making syngas has some level of thermal and carbon inefficiencies (which are due to cooldown, producer gas cleaning, and the removal of steam prior to FTS reactions), but it is quite amenable to the introduction of H_2 process heat and direct H_2 enrichment of syngas just prior to FTS reactions. Although TRI has tail gas from FTS reactions being used in other processes in a biorefinery/pulp plant scenario, the very same tail gas, particularly the unreacted CH_4 and CO_2 components, needs to be recycled to some methane reformer to retain the 100% conversion of biomass carbon to synfuel. The study at Purdue University had a similar suggestion: enrich the syngas and recycle the tail gas as a modification to a generic gasification technology.[2]

We can envision a hypothetical modification of TRI gasification technology that takes advantage of its various unique features (low weight, low footprint, low environmental impact, need for water, need for low biomass contaminants, and so on) for use with seabed harvesting of algae technology. The Ocean Thermal Electric Conversion (OTEC) technology[23] can provide electricity on site, and the sunlight and some drying of algae along with FTS water byproduct can provide direct energy and desalted water feedstock in the photoelectrochemical water splitting concept of generating H_2 fuel (such as that being planned by Coastal Hydrogen Energy, Inc., at a cost of less than $1/kg) at the plant site as co-located with the biorefining of algae. The oil tankers can make periodic visits to load up on the clean Fischer−Tropsch liquids to take to the large land-based oil refineries. Because the liquid hydrocarbons can also be easily converted or refined to methane, the synthetic natural gas can be provided to inland areas for use in fuel cells to generate power, heat, inexpensive H_2 fuel, or potable water. There would be no need for desalination of seawater to obtain fresh water if it can be obtained more economically through the combustion of methane derived ultimately from sunlight, algae, and seawater.

Hydromax Concept. The second gasification concept is the HyrdoMax[24] at the other extreme of very high temperatures (>1000 °C), using FeSn liquid metal alloy as heat and chemical carriers, and would have no need for the external source of water beyond that of green wood. The gasification process is based on pyrometallurgy chemistry, which involves gaseous carbon compounds and water. Some metals, under the right set of conditions, will remove oxygen from H_2O or CO_2 to form a metal oxide with an exothermic release of energy. Of course, to gain access to the unreacted components, a very porous ceramic matrix or a liquid metal that can move the oxides out of the way is required. At some later stage, the metal oxides then undergo endothermic reduction with carbon or hydrocarbons, as in the reaction

$$CH_x + \text{MetalO} \rightarrow \text{Metal} + CO + \frac{x}{2}H_2$$

or the metal oxides can undergo self-reduction as in the reaction

$$\text{MetalO} \rightarrow \text{Metal} + \frac{x}{2}O_2$$

For the endothermic reduction to proceed, we must attain a sufficiently high temperature for the Gibbs free energy to become negative for the particular reaction process.

The HydroMax process, as shown on their website,[24] takes advantage of the pyrometallurgy chemistry of iron. In the first stage, steam is added to oxidize the liquid iron and releases H_2. When the oxide level of iron becomes saturated, the steam is stopped and coal (or biomass) is added to the smelt, to reduce the iron, and CO is released. The process then is cycled back to steam injection. It is a very simple concept but difficult to implement, because of the very high temperature involved and problems with feedstock insertion. We note that this process can easily be adapted to provide biofuel at the 150% biomass energy level by merely adding external H_2 to the syngas and using additional H_2 to combust with O_2 to keep the reaction bath at a very high temperature of 1300 °C. One source of H_2 at very high temperature is HydroSol,[25] whose goal by 2020 is to produce H_2 at a cost of $0.06/kW h, which converts to $2/kg. It uses the shuttering of solar rays to the reaction chamber to achieve the recycling of temperatures between oxidation (800−1000 °C) and reduction phases (>1300 °C). The periodic cycles of both HydroMax and HydroSol can perhaps also be matched so that minimal storage of H_2 and CO is required in the hybrid system. Because both processes involve very high temperatures, the lifetime of the container cladding may be a serious issue. The vision for this hybrid system is for use in regions where (i) water must be conserved, (ii) there is a good supply of mildly moist biomass (i.e., with at least 24% moisture content overall), and (iii) the sun is in view most of the time.

Fast Pyrolysis, Followed by Char Conversion. The third gasification concept for the almost-complete conversion of the biomass carbon involves two stages. The first stage uses fast pyrolysis to create bio-oil, using a special extruder at temperatures of ~500 °C, and the leftover char then is passed to a commercial char converter chamber, using some steam/air injection to create char-derived syngas.[26] This syngas is used in the burner to provide the process heat for the extruder, and the char that still remains is discarded. Although carbon conversion is potentially less than the earlier two processes, it seems to be quite economical, judging from recent company announcements (as reported by DynaMotive Energy Systems Corporation[27]). The conversion of biomass carbon can be enhanced and made suitable for upgraded syngas as follows:

(1) Instead of condensing the producer gas to bio-oil, heat it further to 800 °C to thermally crack the tars to simpler hydrocarbons, CO, H_2O, and CO_2 to create a raw syngas;

(2) Insert external H_2 to combine with H_2O in the char converted chamber and increase it to ~700 °C or higher to obtain much greater char conversion to raw syngas;

(3) Clean the tar, carbon, and contaminants from the raw syngases;

(4) Process the cleaned raw syngases in the 800 °C methane reformer to produce a high-quality syngas without the hydrocarbons;

(5) Enrich the syngas with H_2 for optimum use in FTS reactions; and

(6) Recycle the FTS off-gas into the methane reformer to ensure complete conversion of CH_4 and CO_2.

The thermal and carbon inefficiencies would still be similar to the modified TRI concept, and they probably are applicable just as well for the seabed harvesting of algae. However, because of its very low demand for external water, it would be suitable for in-land regions of the United States. The electrical energy needed for steam electrolysis could easily be powered by windmills in the vicinity.

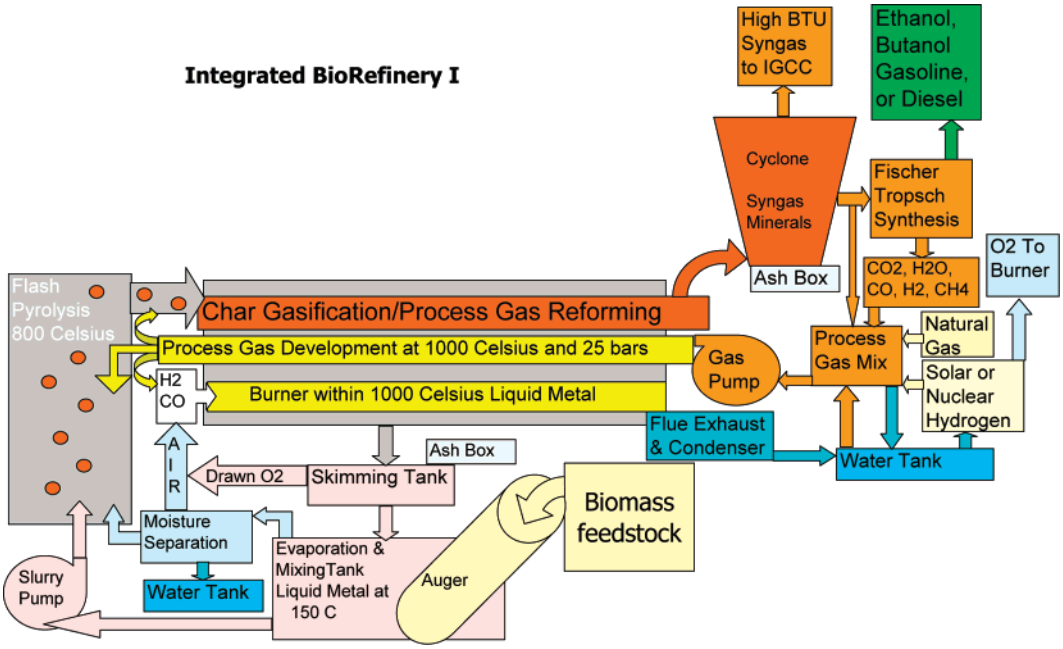

Figure 6. Schematic diagram of integrated biorefinery I concept.

Advantages of Liquid-Metal-Based Gasification

For a new development of unconventional gasification technology, we are looking for the following multistage features: (1) early removal of air and free water from biomass to promote fast pyrolysis during fast heating, a high BTU syngas, and a supply for water splitting into H_2 and O_2; (2) rapid indirect tar cracking to eliminate the gumming of parts; (3) efficient char gasification with minimal H_2O and H_2 augmentation; (4) rapid hydrocarbon reforming without catalysts; (5) reduction of CO_2 by reversing water−gas reactions and increasing H_2 from external sources to improve syngas quality; (6) increasing thermal efficiency, such as eliminating cooldown cycles for syngas cleaning and allowing for heavy insulation; (7) keeping gasification temperatures at <1000 °C, to avoid ash slagging and problems with container integrity; (8) allowing for the recycling of FTS off-gas into the gasifier, to convert the remaining carbon molecules; (9) adaptable to pressure levels, depending on the end use of syngas; and (10) adaptable to any carbon-based feedstock, particularly woody biomass in the chip-sized dimensions. All these features should be met using a low-temperature liquid metal alloy in the following two biorefinery designs.

Direct Contact with Liquid Metal. The first biorefinery concept, which is depicted in Figure 6, involves direct contact with liquid metal. The use of liquid metal as a heat, mass, and reactant carrier is not a new idea: there are numerous related patents, perhaps the earliest one in 1949 by FPL researcher Alfred Stamm.[7] However, in this new design, we are utilizing unique properties of liquid metal to achieve full gasification of feedstock into syngas. Since we realized that we could use wood chips, this finding meant that we could use FPL paper-mill expertise to prepare the biomass feedstock. As for the use of clean, high-BTU syngas, we can use existing commercial devices for the cyclone, the integrated gasification combined cycles (IGCC), and FTS. New developments, requiring both UW−Madison's nuclear reactor expertise and the FPL's biomass expertise, have been made, regarding the gasifier core. The most efficient pyrolysis of wood into volatiles occurs when biomass is first dried in the evaporation tank at low non-degrading temperatures (<200 °C) and then the melt/biomass slurry is injected at high pressure into the flash pyrolysis tank at temperatures of at least 800 °C. The heavy tar trapped in the bubbles will completely thermally crack into simpler molecules without catalysts,[28] thereby removing the tar gumming that is such a problem in several gasifier concepts. With an adequate level of pressure and steam/H_2 insertion, we expect to achieve almost-complete gasification of char and hydrocarbons within the 1000 °C gasification chamber for a reaction time of several seconds.[29,30] Our process also takes advantage of the limited ability of the liquid metal (PbBi or BiSn alloys, which are liquid over a very wide range of temperatures) to absorb oxygen from steam in the flash pyrolysis chamber, which allows more of the hydrogen gas to exothermically react with residual char and tar. Finally, the metal oxide will float on pure liquid metal in the gasification chamber, so that any unreacted char and hydrocarbon can deposit on the oxidized surface to react with it to form CO and reduce the metal. We have included recycling of any unused syngas components, particularly CO_2, CH_4, and CO, as well as the external use of natural gas or the solar/nuclear H_2 gas, into the process gas tube that may contain catalysts to convert the contents to H_2 and CO. We would note the syngas is at the highest BTU level, the highest quality, and the cleanest level possible, because (i) the air is removed early, (ii) the superheated steam is strategically used to gasify the char residue and crack the heavy tar, (iii) the process gas includes the H_2 gas enrichment, and (iv) any combustion was done with the process gas feedstock for an indirect heating of all endothermic processes. Even minor contaminants (such as the sulfur compounds) can be removed by the liquid metal, but that will make the skimming technology quite challenging.

Separation of Feedstock from Liquid Metal. A second biorefinery concept, which is depicted in Figure 7, was devised to handle greater levels of ash in the feedstock, such as agricultural wastes, including animal manure, by not allowing contact between the feedstock and liquid metal. Although this biorefinery methodology involves more low-risk conventional components, it can be distinguished from other gasifiers (i.e., the similar DynaMotive gasifier discussed previously that also can handle higher levels of contaminants, such as those found with disposed treated telephone poles) through the use of liquid

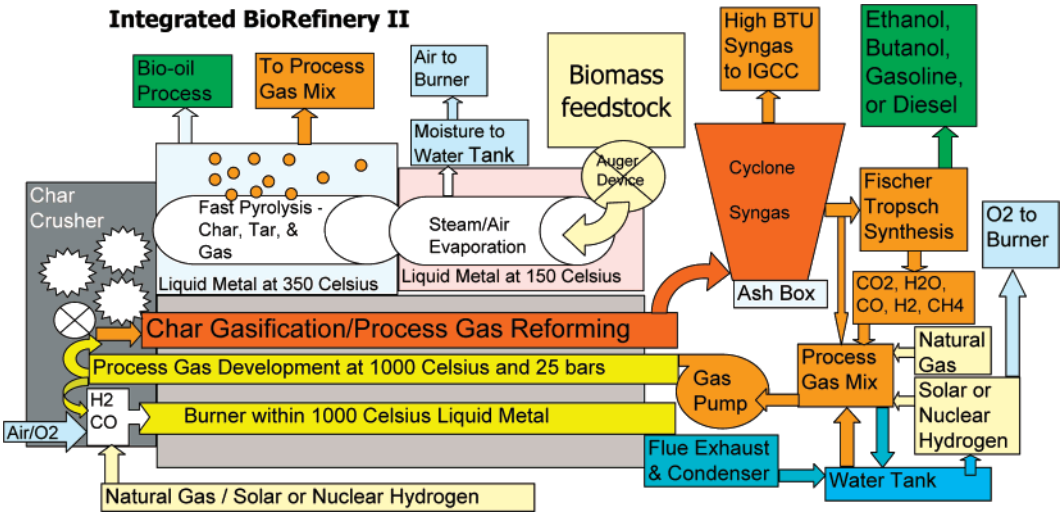

Figure 7. Schematic diagram of integrated biorefinery II concept.

metal as heat carriers to give a much smaller refinery footprint. A possible low-cost option is the production of bio-oil from the condensation of relatively clean tar generated at 350 °C and the production of internal-combustion-engine-ready syngas from the crushed char residue. It might be thought of as the higher-productivity replacement to the anaerobic digesters now used on large dairy farms to generate power and heat. If the object is to build a medium-scale facility (e.g., ~500 dtpd), then the volatiles that consist of tar and noncondensable gas can be mixed with the process gas for relatively much larger production of higher-quality syngas for the lower-cost synthesis of mixed alcohols, of which 80% are converted to ethanol and the other 20% is directed toward electricity/steam (similar to the National Renewable Energy Laboratory (NREL) biorefinery design[31] for a different gasification technology). Although the raw syngas will not be as clean as the first biorefinery concept, it will likely be cleaner than other gasifiers, in terms of soot and tar, and, of course, much ash must be removed through the use of additional cyclones.

We can also visualize co-locating a large-scale biorefinery using the state-of-art FTS liquids and no emission of CO_2 with a nuclear plant redesigned to allow for increased production of H_2 and O_2 gas from the splitting of the water and for use of nuclear waste heat to predry the biomass and provide some process heat. No similar concept was found in the literature. Because the origin of water for splitting into H_2 and O_2 are from biomass water evaporation and FTS byproduct steam, it makes sense to locate the water splitting units adjacent to the biomass gasifier. This also increases the safe use of the H_2, in that it is primarily used and created within the same facility and is located separately from the nuclear plant. At UW−Madison, under DOE sponsorship, they have been studying appropriate heat-transfer fluids flowing between the nuclear reactor and biorefinery that are safe, efficient, and operate at high temperatures. Indeed, certain salts can be used to transfer heat at ~1000 °C directly to the gasification chamber, thereby eliminating the need for an H_2 burner and adding to facility safety. The H_2 can then be used more efficiently to enhance the gasification process, enrich the syngas, and store its energy into the hydrocarbon fuel via FTS. The high-temperature electrolysis or the high-temperature water splitting with the sulfur−iodine cycle are the hydrogen production units that are compatible with nuclear reactors (details can be found on the DOE hydrogen energy website[19]) and also with the liquid-metal-based gasification technology. These are high-throughput units that have the potential of costing less than \$2/kg of H_2 at the plant.

Conclusion

In this paper, we allowed very minimal discussion on the subject of efficiency, for several reasons.

(1) To avoid confusion with the current usage of efficiency. An example is that some biomass gasification technology is quoted as being 70%−80% energy efficient, when, in reality, they are saying that 50% of biomass energy is converted to the biofuel and the remaining useful heat energy is supplied with steam power and heat.

(2) At this time, the required process modeling of heat and mass transfers is not possible, because we do not yet have a continuous pilot scale of the proposed technologies in which to obtain efficiencies data of each component. Initially, we can expect relatively low efficiencies, but it will at least be an improvement over current technologies, as well as have considerable room for future improvements.

(3) The concept of efficiency requires that a considered process is, at most, 100% efficient, which we could have done had we used the percentage of biomass carbon converted to biofuel, but it is not as intuitive as using the percentage of biomass combustion energy, and that biomass energy is best superseded by other forms of non-fossil energy to split water to obtain H_2 and O_2. In addition, it was desired to mark as a reference point in which no combustion of biomass is needed for process heat (because of a less-expensive alternative source for process heat) and in which the energy from hydrogen gas enrichment begins to be added to the energy content of the biofuel.

(4) When the ultimate source of energy is inherently plentiful, as with solar, wind, or even nuclear energy, the main determining factor in their use will be the supply cost (such as the cost per kilowatt-hour, or dollars per kilogram of H_2) and throughput, rather than energy efficiency.

In the final analysis, the discussion of process efficiency is not required to accomplish two main objectives of this paper, which are (i) to bring rationality into the current confusing and perhaps conflicting claims of biofuel productivity, and (ii) bring attention to a potential breakthrough in the producing biofuel with a new gasification technology that has the eight characteristics of biofuel vision, as discussed in the Appendix.

With small Forest Products Laboratory (FPL) grants, the University of Wisconsin at Madison (UW−Madison) has performed small-scale laboratory experiments that verified the flash pyrolysis performance of wood rapidly inserted under various conditions of the liquid metal alloys. Gas absorption issues within the metal alloys have also been investigated. Sufficient data have been collected for the university to submit a patent application. The next stage is to construct the small-scale continuous operating system for the liquid-metal contact version, to show feasibility and allow assessment of economics, including the wells-to-wheels calculations.

Meanwhile, the liquid-metal noncontact version requires development on extruder experimentations for fast pyrolysis at low temperatures, and also experimentations on char crushing in conjunction with its gasification using simulated process gas. Only then can we consider a small-scale continuous version for this second gasification concept, and proceed onward to mass- and heat-transfer process modeling required to show feasibility.

Although research is being conducted nationwide to develop either a biofuel economy or hydrogen economy, there has been some strategic uncertainty in the direction of such work. In the case of biomass gasification approaches to biofuels, we have shown that great potential exists beyond the conversion efficiencies of current gasifiers, and we have provided at least five gasification engineering concepts that could have the potential to triple the current synfuel productivity when H_2 enrichment is in place. Indeed, given the real costs of biomass and hydrogen feedstock supply, this is really the only non-fossil approach that can have any near-term hope of reaching a cost of $1/gal of synfuel at the plant gate to be competitive with coal-to-liquid (CTL) synfuels. We encourage biorefinery researchers and hydrogen energy researchers to work collaboratively and help mutually jump-start the biofuel and hydrogen economy of the future. Indeed, when hydrogen gas becomes more plentiful and inexpensive, biofuel production is really the only near-future marketable option that can absorb the huge amount of hydrogen that will be produced. Meanwhile, biofuel researchers need the hydrogen enrichment concept to help solve the many thorny problems of biofuel production from woody biomass without being forced to develop costly exotic technologies of genetic, catalyst, or nanostructure engineering.

Appendix. Vision Statement for Hydrogen Enrichment for Biomass Gasification

Consider a vision of the biofuel future with the following characteristics:

(1) Synfuels derived from biomass gasification with hydrogen enrichment can *completely satisfy current U.S. transportation fuel needs using available biomass.* Consumption of liquid fuels in transportation is estimated to be ∼200 billion gallons per year in the United States (primarily gasoline, diesel, and aviation fuel). U.S. biofuel production accounts for only ∼2% of the total fuel value of this liquid fuel energy consumption.[21] U.S. fuel ethanol production (from corn grain) was at ∼6 billion gallons in 2006, whereas outputs of bio-diesel and other liquid biofuels were much smaller, and ethanol has only about two-thirds of the energy content per gallon of conventional hydrocarbon fuels. Obviously, a substantial shift in technology will be needed to satisfy current liquid fuel needs with biofuels. According to a recent national report, just over 1 billion dry tons per year of biomass can be supplied sustainably in the United States from the forest and agriculture sectors, albeit at a higher per-dry-ton cost basis as demand and supply are ramped upward.[6] That amount of biomass is sufficient to replace all current liquid transportation fuel needs, but only if the liquid fuels are derived from biomass gasification with hydrogen enrichment.

(2) Production of biofuels via biomass gasification along with hydrogen enrichment will *conserve and extend the biomass resources of the United States*, by achieving the highest possible conversion of carbon from biomass to hydrocarbon and alcohol fuels (∼100% conversion). Conventional biofuel production technologies, including both the biochemical and thermochemical conversion pathways (without hydrogen enrichment), can convert only 33% or less of the carbon in biomass into carbohydrate or hydrocarbon fuels. Most of the carbon in the biomass is wasted, converted to byproducts, or ultimately is emitted as carbon dioxide (CO_2). However, proposed liquid-metal-based gasification of biomass and hydrogen enrichment of the syngas permits the conversion of essentially all of the carbon from the biomass into hydrocarbon fuel (based on stoichiometric analysis). This is because any formed char and tar are largely converted during the liquid-metal-based gasification to carbon monoxide (CO) in syngas, and the enrichment of hydrogen in syngas (higher ratio of hydrogen to carbon) permits essentially all of the carbon from biomass to be converted to hydrocarbon fuel via a Fischer−Tropsch synthesis (FTS) or similar catalytic technology. The hydrogen enrichment also augments the amount of fuel produced, such that ∼3 times as many gallons of biofuel are produced per ton of biomass as in conventional biomass gasification technology, substantially conserving and extending biomass resources of the United States. Although the gasification technology can also convert coal to synfuel, the excessive amount of water needed as a feedstock for this fossil conversion is not needed in the case of moist biomass conversion into hydrocarbon fuel. This also conserves water needed for agriculture and habitats in addition to that needed by the biomass resources in the fresh water regions of the United States.

(3) Hydrogen enrichment of syngas to produce liquid fuels from biomass will *jump-start the future hydrogen and biofuel economy*, by avoiding substantial and costly changes in the current liquid fuel and transportation infrastructures of the United States, and by providing synfuel at prices that are competitive with fossil-based fuels. Presently, hydrogen is essentially not utilized commercially as a fuel for transportation in the United States, partly because of fuel cost considerations, but also simply because hydrogen-fuel vehicles and hydrogen-fuel transportation and delivery systems would require completely different infrastructures (e.g., systems capable of storing and pumping liquid hydrogen under high pressure, and vehicles with engines or fuel cells capable of burning the much-lower-energy-content elemental hydrogen). In addition, the leading conventional biofuel, ethanol, will also require some changes to its infrastructure if its use is to be significantly expanded (e.g., more flex-fuel vehicles and modified transport and storage systems to cope with the hygroscopic nature of pure ethanol). On the other hand, with biomass gasification and hydrogen enrichment, hydrogen can be used to make liquid fuels that are fully compatible with existing fuel and transportation infrastructures of the United States (e.g., alkane fuels that will be direct substitutes for conventional gasoline, diesel, and aviation fuels, and that can be used in existing motor vehicles and aircraft without any modification to vehicles or to the fuel transportation and storage infrastructure of the United States).

(4) Production of biofuels via gasification of biomass *enables use of the lowest-cost biomass resources.* Conventional biofuels

such as fuel ethanol made from corn grain or biodiesel made from soybeans compete for food-crop resources and place market pressures on food and livestock prices. Also, cellulosic ethanol production via hydrolysis and fermentation would compete for fairly clean cellulosic biomass feedstocks, similar to clean bark-free pulpwood chips, or material from more-expensive dedicated biomass crops, such as cultivated switchgrass or short-rotation woody crops. On the other hand, biomass conversion to syngas with hydrogen enrichment is much more flexible, tolerating a broad range and often much less-expensive array of biomass resources. Furthermore, adjustment of the hydrogen input will enable optimal conversion of biomass to hydrocarbon fuel, by adjusting the hydrogen-to-carbon ratio in syngas to achieve maximum fuel yield. This means that a varied range of less-expensive organic feedstocks can be utilized efficiently, such as wood bark wastes, forest residues, wood byproducts, agricultural waste, urban yard waste, and even some municipal refuse biomass waste, as well as any of the more-expensive biomass feedstocks (such as dedicated biomass energy crops). The technology is not at all dependent on genetic modification of the cellulose or lignin content of biomass energy crops and can utilize any form of organic biomass available.

(5) Substitution of biofuels via gasification of biomass *will eliminate the atmospheric carbon emissions that are associated with the use of fossil fuels in transportation*. The carbon emitted to the atmosphere as CO_2 from the combustion of biofuels will be precisely offset by the capture of atmospheric CO_2 by photosynthesis in the growing of biomass used for biofuel production. Carbon will also likely be sequestered in soil via the roots and leaf fall from growing biomass, which suggests the possibility of net negative carbon emissions (carbon capture and storage). The primary air emission from a biofuel refinery based on liquid-metal-based gasification and hydrogen enrichment would be oxygen originated from the wet biomass during the process used to make synfuel. That is, during the gasification stage, the oxygen is largely attached to the carbon as CO, and then the gas-to-liquid synthesis will convert the high H:CO ratio to synfuel and water. This water output, along with the water evaporated from the wet biomass, is transferred to the water splitting unit powered by solar, geothermal, wind, or nuclear energy to provide hydrogen gas for the production of enhanced syngas and the excess oxygen gas is emitted to the atmosphere. In the case of more production of alcohols than alkanes, there would be less oxygen emission. Emissions of unused oxygen in processing will, of course, be balanced by the use of atmospheric oxygen in fuel combustion to CO_2, and the subsequent uptake of CO_2 in photosynthesis, so that the net emissions of carbon and oxygen will be, in effect, zero.

(6) Production of liquid transportation fuels via gasification of biomass *will eliminate sulfur dioxide (SO_2) pollution problems associated with conventional or alternative liquid fuels*. Compared to oil or coal, biomass generally contains very little sulfur; hence, biofuels produced via biomass gasification with hydrogen enrichment will largely eliminate the SO_2 emission problems that are associated with conventional gasoline or diesel fuels, or that could be associated with liquid fuels made from coal.

(7) Economical smaller production units due to the multifunctional nature of liquid-metal-based gasification *will promote homeland security and rural economic development*. Currently, FTS is only economical on large scales, particularly with coal resources; it requires multimillion dollar investment and disruption of the large-scale facility operations can cripple the economy. The economical "green" production of hydrogen will eventually become a reality at smaller scales for effective use by rural organizations. The low-cost biomass supply from wood in particular is expected to be available continuously, because it is not subject to interruptions of growing seasons or is at least storable to compensate for feedstock supply interruptions. This distributed storage supply of biomass feedstock could be potentially much more secure than the U.S. Strategic Petroleum Reserve storage sites (located in salt caverns along the Gulf Coast). The biomass does not need to be shipped over long distances, and synfuel product can be used locally or nationally, adding to its price stability and the reliability that is needed in a rural economy.

(8) Biomass gasification to Fischer−Tropsch liquid fuels may be economically feasible presently without hydrogen enrichment, which suggests the possibility of *developing biomass gasification technology in two phases*. In the initial phase of development, biomass gasification plants could be installed and operated without hydrogen enrichment (using conventional technology for biomass gasification and FTS to produce a synthetic crude product that would be refined to liquid fuels). In a second phase of development, after economical systems are developed to supply hydrogen via the nuclear- or solar-powered electrolysis of water, the gasification plants then could be converted to operate with hydrogen enrichment, and they would produce more-refined liquid fuels with optimal hydrogen-to-carbon ratios for specific end uses, and replace CO_2 emissions by oxygen emissions. It is the higher biofuel productivity that is implied with hydrogen enrichment that can afford the higher per-dry-ton costs implied in the billion-ton-plus supply of biomass, and yet still have the potential to compete with fossil-based fuel prices. The ability to afford the higher per-dry-ton costs will also promote conservation practices such as (i) saving habitats through promotion of tree plantations on unused agricultural land, (ii) reducing wildfire via vegetation thinning in the western United States, and (iii) affecting soil replenishment via rotation between agricultural and energy crops.

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Literature Cited

(1) Alternative Energy from Montana Coal. Available via the Internet at www.business.mt.gov/docs/CTLfuels.pdf.

(2) Agrawal, R.; Singh, N. R.; Ribeiro, F. H.; Delgass, W. N. Sustainable fuel for the transportation sector. *Proc. Natl. Acad. Sci.* **2007**, *104* (12), 4828.

(3) Dietenberger, M. Mechanistic Pyrolysis Kinetics of Solid Redwood Constituents Using a Modified Cone Calorimeter Test. *Fire Saf. J.*, in press, 2008.

(4) Henrich, E.; Dinjus Tar-free, high pressure synthesis gas from biomass. Presented at the Expert Meeting on Pyrolysis and Gasification of Biomass, 2002, Strasbourg, France, Sept. 30−Oct. 1, 2002.

(5) Tillman, D. A.; Rossi, A. J.; Kitto, W. D. Properties of Wood Fuels. In *Wood Combustion−Principles, Processes, and Economics*; Academic Press: New York, 1981; Chapter 2.

(6) Perlack, R. D.; Wright, L. L.; Turhollow, A. F.; Graham, R. L.; Stokes, B. J.; Erbach, D. C. Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply, available via the Internet at http://feedstockreview.ornl.gov/pdf/billion_ton_vision.pdf (last accessed 2005).

(7) Stamm, A. J. Destructive Distillation of Solids in a Liquid Bath, U.S. Patent No. 2,459,550, Jan. 18, 1949.

(8) Butt, D. Formation of phenols from the low-temperature fast pyrolysis of radiatia pine (*Pinus radiata*): Part II. Interaction of molecular oxygen and substrate water. *J. Anal. Appl. Pyrolysis* **2006**, *76* (1−2), 48−54.

(9) Muller, R.; Zedtwitz, P. V.; Wokaun, A.; Steinfeld Kinetic investigation on steam gasification of charcoal under direct high-flux irradiation. *Chem. Eng. Sci.* **2003**, *58*, 5111.

(10) Dietenberger, M. Update for Combustion Properties of Wood Components. *Fire Mater. J.* **2002**, *26*, 255.

(11) Hofbauer, H.; Rauch, R.; Bosch, K.; Aichernig, C.; Koch, R. Biomass CHP-Plant Güssing—A Success Story; Industrielle Kompetenzzentren und Netzwerke, Renet-Austria, Austria, 2002.

(12) Paisley, M. A.; Overend, R. P. Verification of the Performance of Future Energy Resources' SilvaGas Biomass Gasifier—Operating Experience in the Vermont Gasifier. Presented at the Pittsburgh Coal Conference, Sept. 24−26, 2002, Pittsburgh, PA.

(13) Chen, G.; Sjostrom, K.; Bjornbom, E. Pyrolysis/Gasification of Wood in a Pressurized Fluidized Bed Reactor. *Ind. Eng. Chem. Res.* **1992**, *31*, 2764.

(14) Fushimi, C; Araki, K.; Yamaguchi, Y.; Tsutsumi, A. Effect of Heating Rate on Steam Gasification of Biomass. 2. Thermogravimetric−Mass Spectrometric (TG-MS) Analysis of Gas Evolution. *Ind. Eng. Chem. Res.* **2003**, *42* (17), 3929.

(15) Spleithoff, H. Status of Biomass Gasification for Power Production, *IFRF Combust. J.* **2001**, Article No. 200109.

(16) Dry, M. E. High quality diesel via the Fischer-Tropsch process—a review. *J. Chem. Technol. Biotechnol.* **2001**, *77*, 43.

(17) Simonetti, D. A.; Rass-Hansen, J.; Kunkes, E. L.; Soares, R. R.; Dumesic, J. A. Coupling of glycerol processing with Fischer−Tropsch synthesis for production of liquid fuels. *Green Chem.* **2007**, *9*, 1073.

(18) Walsh, M. E. U.S. Energy Crop Economic Analysis: Status and Needs. *Biomass Bioenergy* **1998**, *14* (4), 341.

(19) DOE hydrogen energy website, http://www1.eere.energy.gov/hydrogenandfuelcells/technologies.html.

(20) DOE Annual Energy Review 2006, Report No. DOE/EIA-0384-(2006). Available via the Internet at www.eia.doe.gov/emeu/aer/, posted June 27, 2007.

(21) DOE 2003 gasification technologies report. Available via the Internet at www.fischer-tropsch.org/DOE/DOE_reports/doe_reports_toc-I-R.htm.

(22) TRI website: http://www.tri-inc.net/index.html.

(23) Avery, W. H.; Richards, D. Design of a 160 MW OTEC Plantship for production of methanol. *Oceans* **1983**, *15*, 746.

(24) HydroMax website: www.diversified-energy.com.

(25) HydroSol website: www.solarpaces.org/Tasks/Task2/HYDROSOL2.HTM.

(26) Piskorz, J. Majerski, P.; Radlein, D. RTI Resource Transforms International, Inc. Energy Efficient Liquefaction of Biomaterials by Thermolysis. U.S. Patent 5,278,271, March 17, 1998.

(27) (a) DynaMotive Energy Systems Corp. website and relevant patent: www.dynamotive.com.

(28) Wang, T.; Chang, J.; Cui, X.; Zhang, Q.; Fu, Y. Reforming of raw fuel gas from biomass gasification to syngas over highly stable nickel-magnesium solid solution catalysts. *Fuel Process. Technol.* **2006**, *87*, 421.

(29) Barrio, M.; Gøbel, B.; Risnes, H.; Henriksen, U.; Hustad, J. E.; Sørensen, L. H. Steam gasification of wood char and the effect of hydrogen inhibition on the chemical kinetics. In *Progress in Thermochemical Biomass Conversion*; Bridgwater, A. V., Ed.; Blackwell Science, Ltd.: Edinburgh, U.K., 2001; p 32.

(30) Wu, J.; Fang, Y.; Wang, Y.; Zhang, D. Combined Coal Gasification and Methane Reforming for Production of Syngas in a Fluidized-Bed Reactor. *Energy Fuels* **2005**, *19*, 512.

(31) Phillips, S.; Aden, A.; Jechura, J.; Dayton, D.; Eggeman, T. Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass, Technical Report NREL/TP-510−41168, National Renewable Energy Laboratory, Golden, CO, April 2007.

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